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EMITTANCE STUDIES OF VARIOUS HIGH TEMPERATURE MATERIALS AND COATINGS

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EMITTANCE STUDIES OF VARIOUS HIGH TEMPERATURE MATERIALS AND COATINGS

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Project 281

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I. SUMMARY

This report describes emittance studies of various materials and coatings for materials used in high temperature applications and the development of techniques for improving the emittance of a given structural or high temperature material.

The materials and coatings which were studied included the following:

1. Tantalum with coatings of silicon carbide, pyrolytic graphite, and plasma sprayed cobalt oxide
2. 6AL-4V titanium alloy coated with Rokide C
3. N-155 alloy
4. L-605 alloy sand blasted and coated with plasma sprayed Fe_2O_3
5. Alumina coated with plasma sprayed NiO, MnO_2, and flame sprayed Rokide C
6. Alumina with small additions of Fe_2O_3 and CoO
7. Graphite coated with silicon carbide

Measurements were made in air and in vacuum using specialized equipment. The data which were obtained are presented in three forms: as total emittance, as spectral emittance, and as a composite of the two.

II. INTRODUCTION

Environmental conditions encountered by advanced air-breathing propulsion systems create an ever increasing challenge for materials technology, particularly in the area of high temperature operation. Among the material properties which become important as service temperatures increase, emittance deserves particular attention.

The work reported herein wes devoted to the measurement of emittances of materials and coatings used in high temperature applications and in the development of techniques for improving the emittance of a given structure or high temperature material.

III. ANALYTICAL STUDIES

With the increasing use of refractory coatings for the protection of structural materials exposed to the rigors of hypersonic flight or re-entry, exhaust gases, and other high temperature environments, the thermal properties of these materials must receive an increasing amount of attention. A knowledge of their emissivities (if the surfaces are optically polished) or emittances (if they are not) is invaluable to the calculation of radiant heat transfer. The terms

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emissivity and emittance are used here according to normal convention. The term emissivity is applied as the measure of an intrinsic property of a material while emittance is used in cases where the history and surface treatment of the material may have a pronounced effect on the value. Emisaivity is the lowest limiting value of emittance. The units are dimensionless and can be used interchangeably. The term emittance is, however, more appropriate for engineering materials and will be used in this report whether the surfaces are polished or not.

The control of radiant heat transfer (emittance), can be accomplished by selection of proper coatings with desirable thermal properties and/or by treatment of the surfaces by other processes such as oxidation, sandblasting, etc., and may effectively extend the temperature range over which a given structural material can be used.

A black body, at thermal equilibrium with its surroundings, i.e., at the same temperature, absorbs all of the radiation it receives. In order to remain at equilibrium, it must radiate the same amount of energy as it absorbs. A non-black body in equilibrium with its surroundings, reflects a portion of the radiation reaching it, transmits a portion if it is not opaque, and absorbs the remainder. It also emits the same amount it absorbs. If the body is not at the same temperature as its surroundings, it will emit more or less than it absorbs in order to approach equilibrium. The rate at which the body tends to reach equilibrium is an indication of the value of its emittance. The fraction of energy emitted by a body, when compared to the energy emitted if it were a black body, is the emittance value of the body. Thus

$$\epsilon = \frac{W'}{W} \qquad (1)$$

Where

ϵ = Emittance

W = Hemispherical radiant intensity for a black body, watts/cm^2

W' = Hemispherical radiant intensity of a non-black body, watts/cm^2

Heated bodies radiate a broad spectrum of energies which, for a bleck body, are distributed as shown in Figure 1. As the temperature of a black body increases, the wave length at which radiation is maximum decreases and the distribution of the energy radiated shifts toward the blue end of the spectrum. Even with this shift, it is only at very high temperatures that an appreciable amount of the energy radiated is visible. For example, an ingot of iron at 1800°F radiates only about 0.0065 percent of its emitted energy in the visible (0.4 to 0.7 micron) portion of the spectrum. Even the sun, at about 10,000°F, emits only about 35 percent of its energy as light. Total emittance then is the ratio of the total thermal energy radiated by a given body, to that radiated by a black body at the same temperature. The spectral emittance is this ratio taken at a specific wave length.

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(For this reason, total emittance is a better indicator of the radiant heat transfer behavior. This is especially true if the wave length used in in the visible part of the spectrum as is the case with optical pyrometers. However, the use of an optical pyrometer in emittance measurements has a particular advantage in that measurements can be made on non-oxidizable materials under oxidizing conditions, similar to that which might be encountered in an actual situation, with a maximum of simplicity and in a minimum amount of time.)

The calculations of emittance values can be made quite readily from optical and radiation pyrometer data by making use of a graph (Figure 2) which has been prepared for this purpose. This graph makes use of two basic laws governing radiation, namely: Planck's spectral distribution law, and the Stefan-Boltzmann fourth-power law.

Planck's law:

$$W_\lambda = \frac{C_1}{\lambda^5 \left(e^{C_2/\lambda T}-1\right)} \qquad (2)$$

Stefan-Boltzmann law:

$$W_{o\ -\infty} = \sigma T^4 \qquad (3)$$

Where

W_λ = Hemispherical radiant intensity of a black body at wave length, λ, watts/cm^2

$W_{o\ -\infty}$ = Hemispherical radiant intensity for all wave lengths, watts/cm^2

λ = Wave length, μ (microns)

T = Absolute temperature, °K

C_1 = First radiation constant = 3.7413×10^4, watt μ^4/cm^2

C_2 = Second radiation constant = 14,388, μ °K

σ = Stefan-Boltzmann constant = 5.669×10^{-12}, watts/cm^2 T^4

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Planck's Equation can be extended to non-black bodies (References 1 and 2) giving

$$W'_\lambda = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} \tag{4}$$

$$= \frac{C_1}{\lambda^5 (e^{C_2/\lambda T_{i.o.}} - 1)} \tag{5}$$

Where

ϵ_λ = Normal spectral emittance at wave length λ

W'_λ = Hemispherical radiant intensity of a non-black body, watts/cm^2

$T_{i.o.}$ = Indicated optical pyrometer temperature, absolute °K

For the actual temperature,

$$T = \frac{C_2/\lambda}{\ln\left[\epsilon(e^{C_2/\lambda T_{i.o.}} - 1) + 1\right]} \tag{6}$$

The values for this expression were plotted for various values of ϵ and appear as solid lines in Figure 2.

The Stefan-Boltzmann fourth power law can be extended to non-black bodies (Reference 3) to give

$$W'_{o-\infty} = \epsilon_T \sigma T^4 = \sigma T^4_{i.r.} \tag{7}$$

and

$$\epsilon_T = \frac{T^4_{i.r.}}{T^4} \tag{8}$$

or

$$T = \frac{T_{i.r.}}{\epsilon^{1/4}} \tag{9}$$

Where

$W'_{o-\infty}$ = Hemispherical radiant intensity of a non-black body, watts/cm^2

$T_{i.r.}$ = Indicated radiation pyrometer temperature, °K

ϵ_T = Total normal emittance

The dashed lines of Figure 2 were derived from Equation (9).

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The emittance values described in this report as total emittances would be more properly called "band emittances". This is because quartz windows in the optical system absorb part of the emitted energy. Quartz is very transparent to ultraviolet and visible radiations and to infrared up to a wave length of approximately 3.5 microns. Assuming a sharp cutoff at 3.5 microns and complete transmission below this value gives a transmission of 25 percent at 1340°F, 38 percent at 1700°F, 49 percent at 2060°F, 57 percent at 2420°F, 71 percent at 3140°F and 81 percent at 4040°F. It can be seen that the radiant intensity falling in this bank (W_o - 3.5μ) increases with increasing temperatures and approaches W_o - ∞ at sufficiently high temperatures. However, since considerable data have been published which present emittance values measured by similar methods as total emittance or emissivity, this convention will be followed in this report.

Emittances can be calculated graphically as indicated in Figure 2 by knowing the temperature as indicated by an optical pyrometer with a 0.65 micron filter and by a total radiation pyrometer. The optical and radiation measurements made in an oxidizing environment, using the apparatus shown in Figures 3 and 4, were converted to emittances using this graphical technique.

It should be noted that emittances calculated using this technique are correct only if the specimen is a gray body. A gray body is defined as one which has the same emittance over the entire spectral range. The spectral emittance of such a body would equal its total emittance. A black body is also a gray body, but the reverse may not be true. Possible errors that may result in the use of non-gray bodies are discussed more fully in the discussion of results.

The graph (Figure 2) is also useful for calculation of spectral and total emittances of materials for which actual temperature aa well as indicated temperatures are measured. Emittances for the metal samples have been determined by using the solid $T_{i.c.}$ versus T lines for spectral values and the broken $T_{i.r.}$ lines for total values.

IV. MATERIAL SELECTION AND SPECIMEN PREPARATION

The materials investigated in this study are listed in Table I, together with the thickness of the coatings and the surface roughness of the specimens. The surface roughnesses were measured on a profilometer and are presented as conventional RMS values in microns. The alumina (Al_2O_3) samples with 2.0 percent Fe_2O_3, 0.5 percent Cr_2O_3, or 1.0 percent CoO added, together with a sample of Al_2O_3 were obtained from the Coors Porcelain Company. These specimens were fabricated by cold pressing and sintering. The specimens were flat disks, one inch or more in diameter with thicknesses of 1/8-inch or greater, and they provided a sufficiently large target area for pyrometry measurements.

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Another set of alumina specimens, with purities greater than 99 percent, which were fabricated by cold pressing and sintering, were obtained from Western Gold and Platinum Company. These specimens were approximately 1 1/2 inches in diameter and 1/16-inch thick. One of these disks was tested in the as received condition for comparison. Other specimens were coated with flame sprayed Rokide C, which is primarily Cr_2O_3 (See Table II for the composition), and plasma sprayed MnO_2 and NiO. A graphite specimen coated with vapor deposited silicon carbide was prepared for testing in air. This specimen had a very rough surface as can be seen from Figure 5 (which alao shows other typical specimens) and it was approximately 1 1/2 inches in diameter with a coating thickness of about 1/8 inch.

A tantalum specimen was also coated with silicon carbide for testing in the vacuum setup shown in Figures 6 and 7. This coating was applied in the vapor deposition laboratory bell jar equipment shown in Figure 18. An area, approximately 1/8 inch in diameter, on the specimen was protected from coating by placing a disk of graphite, 3/32 inch in diameter by 1/8-inch thick, at the point on the specimen where the thermocouple was to be attached. Also deposited on tantalum specimens were pyrolytic graphite and plasma sprayed cobalt oxide (CoO). The pyrolytic graphite was deposited using the bell jar system discussed previously. Cobalt oxide and iron oxide (Fe_2O_3), were plasma sprayed on specimens of Haynes alloy 25 (L-605), and manganeae dioxide (MnO_2) and nickel oxide (NiO) were plasma sprayed on the alumina specimens. The specimens were roughened on both sides by grit blasting with 20RA silicon carbide and then coated by plasma spraying. The plasma spray powders were prepared by drying and screening the reagent grade powders to the necesaary particle size. A mixture of argon plus 10 percent hydrogen was used as the ionizing gas. The thickness and roughness of the surfaces tested are shown in Table I.

To evaluate the effect of surface condition or roughness, two other surfaces were tested, sandblasted, and oxidized. The materials used for these studies were Haynes alloy 25 (L-605) and Haynes N-155 "Multimet". The surfaces to be evaluated were oxidized by heating in air at about 2000°F for 2 minutes. These specimens were also tested with poliahed surfaces to permit compariaon of results. The metallic specimens were 3/4 inch wide and 4.0 to 5.0 inches long with thicknesses as follows: Haynes alloy No. 25 (L-605) 0.065 inches; 6AL-4V titanium alloy 0.050 inchea, Haynes N-155 "Multimet" 0.050 inches, and tantalum 0.020 inches. The surface condition and/or coatings applied to the metallic alloy specimens are presented in Table I, and the chemical compositions of these materials are shown in Table II.

V. EXPERIMENTAL TECHNIQUES

A. Measurements in Air

All of the alumina specimens, with and without the added constituents, and the silicon carbide coated graphite, were tested in the equipment shown in Figures 3 and 4. With this equipment, the samples were heated by an oxyacetylene torch and the temperatures were measured with an optical pyrometer and a radiation pyrometer. The optical pyrometer used was a Pyrometer Instrument Company, Inc., Micro Optical Pyrometer, and the radiation pyrometer was a Model 8861C Ray-O-Tube manufactured by Leeds and Northrup. The Micro Optical Pyrometer measures energy emitted at a wave length of 0.65 microns.

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The temperature variation of the specimens was accomplished by adjusting the distance between the torch and the specimen. This distance, (for most specimens) varied from 3 to 3 1/2 inches. The flame impingement angle to the surface of the specimen was approximately 45° from the normal. This angle was used to keep the volume of flame in the pyrometer path to a minimum while retaining sufficient impingement to reach the required temperatures.

B. Measurements in a Vacuum

The metallic specimens were tested on the equipment as shown in Figures 6 and 7. The specimens were prepared so that the ends, which make contact with the electrodes, were clean and bright. It was required that the specimens make good thermal as well as electrical contact at both electrodes to insure a relatively uniform temperature distribution in the center. Cleaning was accomplished (in the case of the silicon carbide coatings on graphite) by sandblasting the ends after masking of the central portion of the sample. The specimens of Haynes alloy 25, which were somewhat thick for the slots in the electrodes, were ground to a snug fit. The other specimens were shimmed with copper foil to fit properly. A small area, about 1/8-inch in diameter, was cleaned on the center of the back of each specimen for mounting of a thermocouple. In the case of silicon carbide, this was accomplished during the coating process as previously described. The other specimens were prepared using a spot grinder. Care was taken to place this clean spot in the center of the specimen for maximum temperature uniformity.

The thermocouple material used for these measurements was tungsten versus tungsten plus 26 percent rhenium, usable up to approximately 5000°F and beyond the highest temperatures attempted in this study. It was found that the tungsten/tungsten-rhenium thermocouple was a satisfactory choice for these measurements since it does not form eutectics with melting points lower than the melting points of any of the materials tested.

The thermocouple wires (which were 0.010-inch in diameter) were spot welded to the clean area in the center of the specimen, as close to the midpoint between the electrodes as possible. They were attached to the specimens with both leads the same distance from the electrodes to avoid a-c pickup. The attachments are very important in obtaining reliable measurements and some experimentation was necessary to make adequate bonds. The thermocouple emf was measured by a Leeds and Northrup Model 8686A Potentiometer.

The vacuum system (shown in Figure 6) consisted of a base plate with vacuum line connected to a 13 cfm vacuum pump, argon valve, thermocouple-type pressure gage, water-cooled heating electrodes, and thermocouple leads, all connected by appropriate vacuum seals. This was enclosed in a Pyrex bell jar, with special 1 1/2-inch inside diameter side chambers fitted with 1/4-inch thick quartz windows, resting on a Parker Gask-O-Seal.

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The Ray-O-Tube radiation pyrometer was located about 18 inches from the specimen and required a target diameter of about 0.6-inch at that distance. The alignment of the Ray-O-Tube is critical in that it must be centered in front of the quartz window with its optical axis parallel to the axis of the side chambers and it must be centered on the specimen. The Ray-O-Tube radiation pyrometer and the thermocouple were positioned at the same location but on opposite sides of the sample. The output of the Ray-O-Tube was read on an adjustable range recorder with full scale equal to 2 mv, corresponding to an indicated temperature of 2727°F. The Micro Optical pyrometer and Ray-O-Tube were calibrated against a black body furnace.

The general procedure in a test run was as follows: After the specimen was located in position between the electrodes, the bell jar was attached and carefully aligned with the Ray-O-Tube. The chamber was evacuated to approximately 5 microns of mercury, back filled with argon, and evacuated again. After a second argon purge, the system was evacuated to approximately 3 to 4 microns of mercury. The specimen heating was accomplished by a 4 volt, 10 KVA, a-c power supply. The specimen was heated in increments, and the temperature was allowed to reach equilibrium prior to each emittance measurement.

VI. EXPERIMENTAL RESULTS

The data obtained under this program are presented in three forms: As total emittance, as spectral emittance, and as a composite of the two. The total and spectral emittances were obtained for each of the metallic specimens and composite values were obtained for the materials tested in an oxidizing air environment. The measurements were made over a range of temperatures.

The total and spectral emittance values are considered together since the two values were measured simultaneously on each of the metallic specimens.

A. Tantalum with Coatings of Silicon Carbide, Pyrolytic Graphite, and Plasma Sprayed Cobalt Oxide

The total emittances and spectral emittances (Figures 8 and 9) respectively, are presented for tantalum with a highly polished surface and tantalum coated with silicon carbide, pyrolytic graphite, and plasma sprayed cobalt oxide. The experimental values of total emittance for the polished metal agree with published values (Reference 4), being approximately constant at about 0.25 over most of the temperature range (1900° to 3800°F) with a broad peak of 0.36 at 2400°F. The published data show the values ranging from 0.05 to 0.30 for the temperature range from ambient temperature to 4580°F. The lower and very high temperature ranges were not evaluated in this program. The spectral emittance values obtained show a decrease from 0.6 to 0.4 except for the peak of 0.69 at 2400°F. This result agrees quite well with the published values of 0.55 to 0.36 for the temperature range of 68° to 4580°F. Silicon carbide was found to have a very dramatic effect on emittances. The range of total and spectral values increased to 0.9 to 0.98 and 0.88 to 0.99, respectively. The pyrolytic graphite coating also significantly increased the emittance range values to 0.62 to 0.75 for total emittance and to 0.67 to 0.86 for spectral emittance. The dropping values at the upper end of the spectral emittance curve (Figure 9) were due to a partial loss of the coat-

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ing. The plasma spraying of cobalt oxide apparently reduced the oxide, at least partially, to metallic cobalt. The plasma sprayed material has a fairly high emittance, however, being in the 0.7 to 0.8 range for total emittance and about 0.75 to 0.9 for spectral emittance. The curves (as shown in Figures 8 and 9) drop sharply at a temperature of approximately 2600°F. This is close to the melting point of cobalt (2723°F), at which point the coating apparently flowed and lost its surface texture. At approximately 3400°F, the measured emittances approached those of polished tantalum.

B. 6AL-4V Titanium Alloy Coated with Rokide C

The values of total emittance (ϵ_t) and spectral emittance (ϵ_λ) of the polished metal (Figures 10 and 11) remained fairly constant over the temperature range studied. ϵ_t varied from 0.27 to 0.33 and ϵ_λ ranged from 0.51 to 0.55. A coating of Rokide C significantly increased the emittances to the extent that the ϵ_t values were found to range from 0.72 to about 0.85 while the ϵ_λ values ranged from 0.7 to a high of 0.96.

C. Haynes Multimet N-155 Alloy

The experimental emittance values of polished N-155 alloy were found to be essentially constant over the temperature range selected, with the values increasing slightly at the higher temperatures. This upward trend at the higher temperatures is believed due to recrystallization of the metal and consequent alteration of the surface. Total emittance (ϵ_t) and spectral emittance (ϵ_λ) were measured over the temperature range selected as 0.21 to 0.25, and 0.39 to 0.4, respectively, and are shown in Figures 12 and 13. A slight amount of discoloration appeared on the surface upon heating of the above specimens due to the oxidation resulting from minute amounts of residual oxygen in the vacuum bell jar. The temperature was increased to about 2200°F and the discoloration disappeared. The temperature was reduced and the surface remained bright. Measurements were then taken as indicated in the second cycle curve. Oxidation of the surface, accomplished by heating the specimens in air for two minutes at 2000°F, resulted in a considerable increase in the emittance values. The values increased initially, then dropped off as the temperature approached the melting point of the material. This is believed due to evaporation in a vacuum of some of the surface metal thus carrying away the oxidized coating. The values of total emittances of the oxidized specimens ranged from 0.72 to 0.78, while values for ϵ_λ ranged from 0.71 to 0.85, respectively. These curves are also presented in Figures 12 and 13.

D. Haynes Alloy 25 (L-605) Sand Blasted and Coated with Plasma Sprayed Fe_2O_3

The curves of total and spectral emittance for Haynes Alloy 25 are shown in Figures 14 and 15. As shown in both curves, the values for the polished metal are initially quite high, approximately 0.4 and 0.7, respectively at 1800°F. As the temperature was increased, these values dropped to a relatively low value, approximately 0.26 for ϵ_t and 0.4 for ϵ_λ for a range of temperatures between 2000° and 2400°F. The initial oxidation of the surface, resulting from residual oxygen in the system, is believed acccuntable for the high initial emissivity values. The decrease in values occurring at approximately 1900°F is believed due to the removal

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of the oxide film by either evaporation of the substrate metal or sublimation of the oxide film. The changes of the surface were readily noted when viewed through the optical pyrometer. The emittances remained at their low value when measurements were taken for descending temperatures. It is interesting to note the comparison of behavior between this material snd the N-155 alloy material. Sandblasting the surface increased the total emittance at the higher temperature ranges to approximately 0.35 and the spectral emittance values to approximately 0.6. These increases are rather modest, yet they are significant, considering the simplicity of the surface treatment. Plasma spraying of an iron oxide (Fe_2O_3) coating increased emittance values considerably. The emittance values increased with temperature, ϵ_t ranging from 0.74 to 0.88 snd ϵ_λ ranging from 0.75 to 0.96 over the temperature range (up to 2100°F) selected. No loss of coating was noted in these tests, probably because the coatings were thick enough to prevent evaporation of the substrate.

E. Alumina Coated with Plasma Sprayed NiO, MnO_2, snd Flame Sprayed Rokide C

The results obtained from this phase of the program are shown in Figure 16. These measurements were made using an oxyacetylene torch as the heat source since the specimens could not be heated by passing electrical current through them in the bell jar equipment. The results, calculated graphically as previously described, yielded an emittance value which is a composite of spectral and total emittance. A value of about 0.17, which remained quite constant over a wide temperature range, was obtained for pure alumina. The low emittance of alumina makes this measurement very susceptible to experimental errors. The values lie, however, in the region reported in the literature (Reference 5). The addition of a plasma sprayed coating of Rokide C increased the composite emittance value to 0.73 at 2100°F and the value increased to 0.8 at 2550°F. The emittance was increased to somewhat higher values in the cases of plasma sprayed NiO and MnO_2. Inspection of the specimens after the runs showed a slight fading in the deep brown color of the MnO_2 coating, whereas the NiO had changed from its original black color to a brownish green and also indicated some diffusion into the alumina to produce a bright green color.

F. Alumina with Small Additions of Fe_2O_3, Cr_2O_3, and CoO

These measurements were also made in air and the emissivity values were calculated by the same technique as that used for the previous set of alumina specimens. The values were obtained at specified temperatures and the results are tabulated in Table III. The addition of 2.0 percent Fe_2O_3 significantly increased the composite emittance at a temperature of 3470°F, from a value of 0.29 without additive to a value of 0.58 at a slightly higher temperature. The addition of 0.5 percent of Cr_2O_3 produced nearly the same composite emittance as untreated alumina at 3470°F and gave a much lower value at 3200°F. This lower value was obtained on a smoother surface which had not been heated to a high enough temperature to be thermally etched. In this case, the emittance value was apparently dominated by surface roughness rather than by the addition of Cr_2O_3. The addition of 1.0 percent CoO caused a negligible increase in emittance which was within the limits of experimental error.

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G. Graphite Coated with Silicon Carbide

The composite emittance values determined for this sample are shown in Figure 17. The primary purpose of this phase of the test program was to determine the emittance of silicon carbide in air. The concurrent extraction of information as to the usefulness of SiC as a protective oxidation coating for graphite is of major importance to the advanced materials research program. The low value of emissivity obtained (about 0.75 as compared with published values of 0.88 to 0.92 as denoted in Reference 4) is believed due to the low angle of incidence of the torch (about 25 degrees from normal) used in this measurement. This potential source of error in measurement will be discussed in the conclusions to this report. At the maximum temperature of this test (3300°F), there was no discernible change in the condition of the surface during the 10 to 15 minutes the specimen was held at this temperature nor was any oxidation of the graphite evident.

VII. DISCUSSION OF RESULTS

The various methods and techniques employed in this program to improve the radiant heat transfer characteristics of various materials and material combinations, have resulted in varying degrees of success ranging from definitely negative, for the addition of small percentages of CoO and Cr_2O_3 to Al_2O_3, to very successful for the silicon carbide coating on tantalum. In all of the specimens studied, the application of coatings resulted in some degree of increase in emittance over that of the substrate. The nature of the substrate in some cases influenced the emittances of coated materials. This can be seen in Figure 8 in which the silicon carbide and CoO coatings reflect the peak of about 2400°F in the curve for polished tantalum. The pyrolytic graphite, which is opaque to the wave length of energy emitted, has a flat curve in this region. As might be expected, sandblasting and surface oxidation both increased emittance values. Sandblasting of Haynes 25 alloy caused an increase, although not as marked as the change some materials exhibit upon sandblasting. Oxidizing N-155 alloy produced a coating rich in the oxides of iron, cobalt, nickel and chrome, all of which have high emittances. The emittances of the 6Al-4V titanium alloy, Haynes N-155 Multimet, and Haynes 25 alloy, measured in vacuum, were in good agreement with published data as indicated in References 6, 7, and 8, respectively. The total emittance values for Rokide C increased slightly with temperature from 0.72 to 0.85. This range agrees quite well with values reported by other observers (Reference 9), although these data show a decrease with increasing temperature from 0.86 to 0.74.

It can be seen that the composite emittance for Rokide C coated on alumina and measured in air, was considerably lower than the values for coatings of Rokide C obtained in a vacuum. This is also true for silicon carbide. These low values were apparently due to the presence of the flame in the line of sight of the radiation and optical pyrometers. The oxyacetylene flame, being much hotter than the specimen, emits more energy in the visible portion of the spectrum, to which the optical pyrometer is sensitive. The radiation pyrometer, on the other hand, being not so sensitive to changes in the spectral distribution of energy as to its intensity, is not affected to a great extent by the flame. This results in a wider gap between indicated readings and hence in low apparent values. It also yields temperature values which are higher than they should be. Some error can also be experienced in this type of measurement if the material is not a gray body.

If the total emittance is higher than the spectral emittance, the graphically determined true temperature is lower than it should be and, therefore, the emittance is higher than it should be. If the spectral emittance is greater than the total emittance, these errors are reversed. Further error can be caused by the fact that the temperature of the specimen is not uniform, the center being hotter (by as much as 100°F in some cases) than the edges. Even taking an average temperature leaves considerable uncertainty in the values. Obviously, this method is not one that should be used to obtain highly accurate absolute emittance values. It retains its value, nevertheless, as a useful engineering tool, where comparisons are of interest, and in measuring values under conditions which may be met in actual situations.

The improvement of emittance by the addition of small amount of minor constituents to a refractory matrix is an area requiring further investigation. The work presented in this report was limited to the addition of a singular percentage of each of three high emittance oxides to alumina. Although two of these added constituents (cobalt oxide and chromic oxide) had negligible effects on the emittance values, it is possible that higher percentages would increase the emittance values significantly. The addition of ferric oxide significantly improved the emittance of alumina and it is possible that even higher percentages might improve the valuea even more. Further studies should, therefore, include the investigation of the effects of varying concentrations of additives on the emittance. They should also include a study of the physical effects of adding minor constituents. These might include melting point, coefficient of expansion, and thermal conductivity. The work could be extended to the investigation of these mixtures as coating materials.

VIII. REFERENCES

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6. Defense Metals Information Center Memorandum 91, "The Emittance of Titanium Alloys", W. D. Wood, H. W. Deem, and C. F. Lucks, March 1961.

7. Defense Metals Information Center Memorandum 111, "The Emittance of Stainless Steels", W. D. Wood, H. W. Deem, and C. F. Lucks, June 1961.

8. Defense Metals Information Center Memorandum 119, "The Emittance of Iron, Nickel, and Cobalt and Their Alloys", W. D. Wood, H. W. Deem, and C. F. Lucks, July 1961.

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TABLE I

SUMMARY OF EMITTANCE SPECIMENS

Material	Surface Treatment or Coating	Coating Thickness (in.)	Surface Roughness (μ RMS)
Alumina (1)	As received	--	65
Alumina (1) plus 2.0 percent Fe_2O_3	As received	--	65
Alumina (1) plus 0.5 percent Cr_2O_3	As received	--	65
Alumina (1) plus 1.0 percent CoO	As received	--	65
Alumina (2)	As received	--	30 to 35
Alumina (2)	Flame sprayed - Rokide C	0.004	30 to 45
Alumina (2)	Plasma sprayed MnO_2	0.003	200 to 240
Alumina (2)	Plasma sprayed NiO	0.002	70 to 80
Tantalum	Polished	--	0.5 to 1
Tantalum	Vapor deposited silicon carbide	~0.003	80 to 110
Tantalum	Vapor deposited pyrographite	0.0008	5
Tantalum	Plasma sprayed CoO	~0.0005	30 to 45
Haynes "Multimet" N-155	Polished	--	1 to 2
Haynes "Multimet" N-155	Oxidized	--	1 to 2
Alloy Ti-6AL-4V	Polished	--	2 to 3
Alloy Ti-6AL-4V	Flame sprayed Rokide C	0.004	30 to 45
Haynes Alloy 25	Polished	--	0.7 to 1
Haynes Alloy 25	Sandblasted	--	70 to 90
Haynes Alloy 25	Plasma sprayed Fe_2O_3	0.001	30 to 45
Graphite	Vapor deposited silicon carbide	~1/16	--

(1) These samples were obtained from Coors Porcelain Company

(2) These samples were obtained from Western Gold and Platinum Company

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TABLE II

CHEMICAL COMPOSITION OF MATERIALS

Element	Haynes N-155 Alloy (Multimet) (% by weight)	Haynes Alloy 25 (L-605) (% by weight)
Nickel	19 to 21%	9 to 11%
Cobalt	18.5 to 21	Balance
Chromium	20 to 22.5	19 to 21%
Tungsten	2 to 3	14 to 16
Niobium, tantalum	0.75 to 1.25	--
Molybdenum	2.5 to 3.5	--
Manganese	1.0 to 2.0	1 to 2
Copper	0.5 max.	--
Silicon	1.0 max.	1.0
Sulfur	0.03 max.	--
Phosphorus	0.04 max.	--
Nitrogen	0.1 to 0.2	--
Iron	23.98 to 36.15	3
Carbon	0.08 to 0.16	0.05 to 0.15

Element	Titanium Alloy 6Al-4V (% by weight)
Aluminum	5.5 to 6.5
Vanadium	3.5 to 4.5
Carbon	0.1 max.
Iron	0.3 max.
Nitrogen	0.05 max.
Hydrogen	0.0125 max.
Oxygen	0.15 max.
Titanium	Balance

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TABLE II (Continued)

Element	Rokide C Norton Typical Analysis (% by weight)
Cr_2O_3	82.94
SiO_2	8.39
AL_2O_3	3.16
MgO	2.96
CaO	1.28
Fe_2O_3	0.78
TiO_2	0.16
Na_2O	0.28

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TABLE III

SUMMARY OF EMITTANCE MEASUREMENTS

Sample Number	Composition	Temperature (°F)	Emittance (ϵ)	Notes
1	AL_2O_3	3470	0.29	Surface etched
2	AL_2O_3 + 2.0% Fe_2O_3	3710	0.58	Surface fused
3 (Front)	AL_2O_3 + 0.5% Cr_2O_3	3480	0.28	Surface etched
		3200	0.17	--
(Back)		3200	0.17	--
4	AL_2O_3 + 1.0% CoO	3580	0.33	Surface etched

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RELATIVE SPECTRAL INTENSITY AS A FUNCTION OF WAVE LENGTH FOR A BLACK BODY

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Reference: R-11207

FIGURE 1

MAC 1673

Reference: R-9699A

FIGURE 2

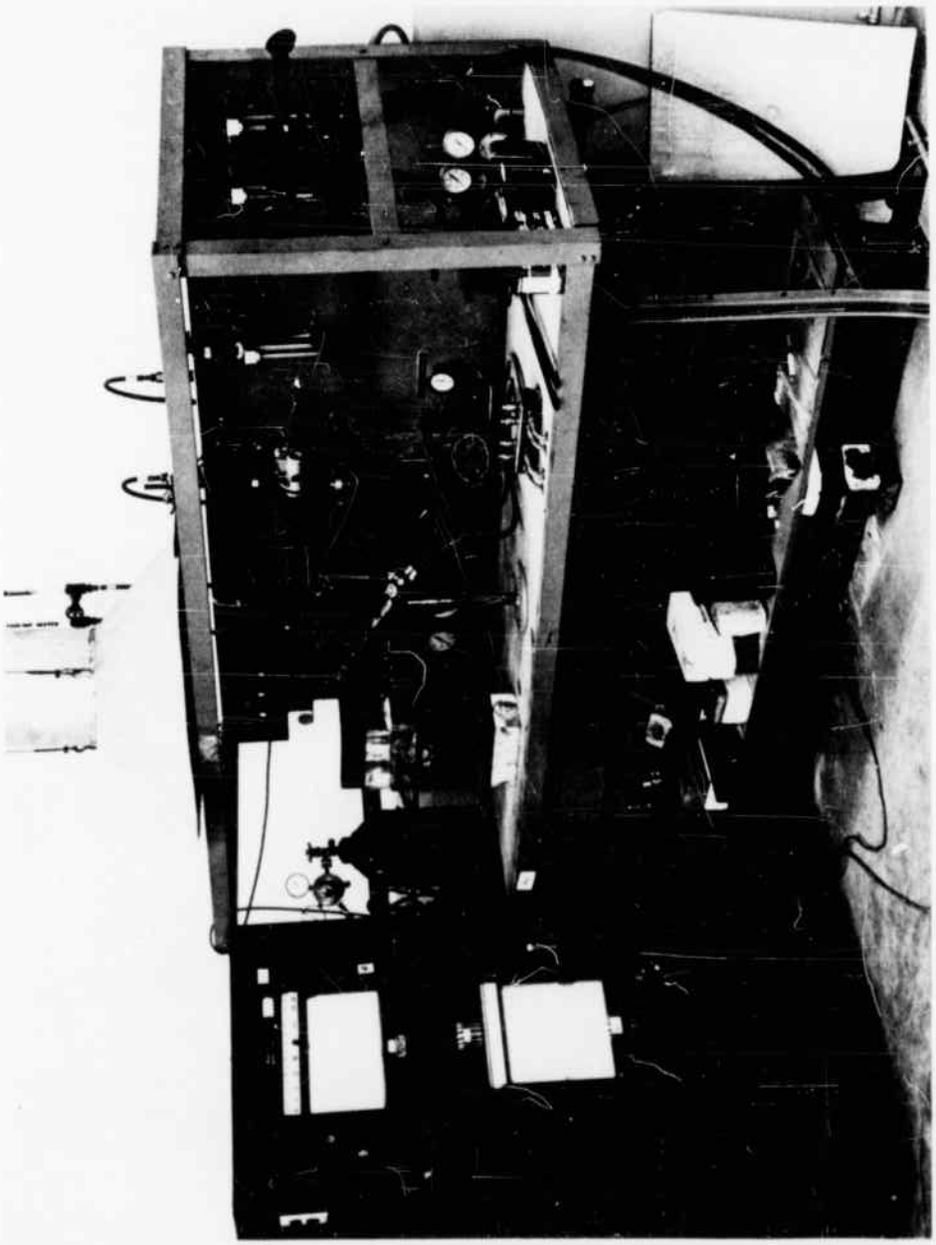

FIGURE 3 - Equipment for Measurement of Emittances in an Air Environment

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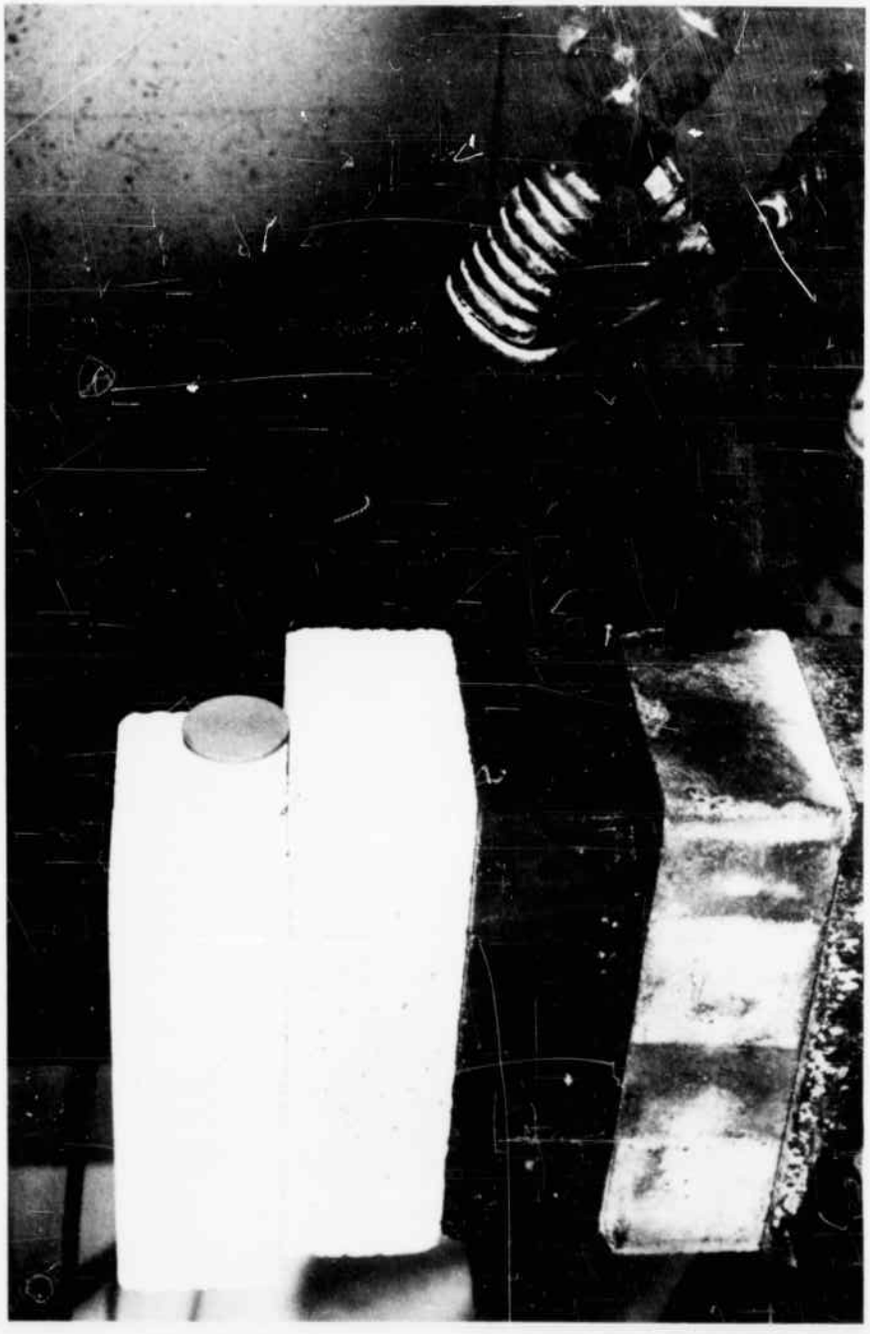

FIGURE 4 - Specimen Installation for Measurement of Emittances in an Air Environment

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Reference: R-111 '5

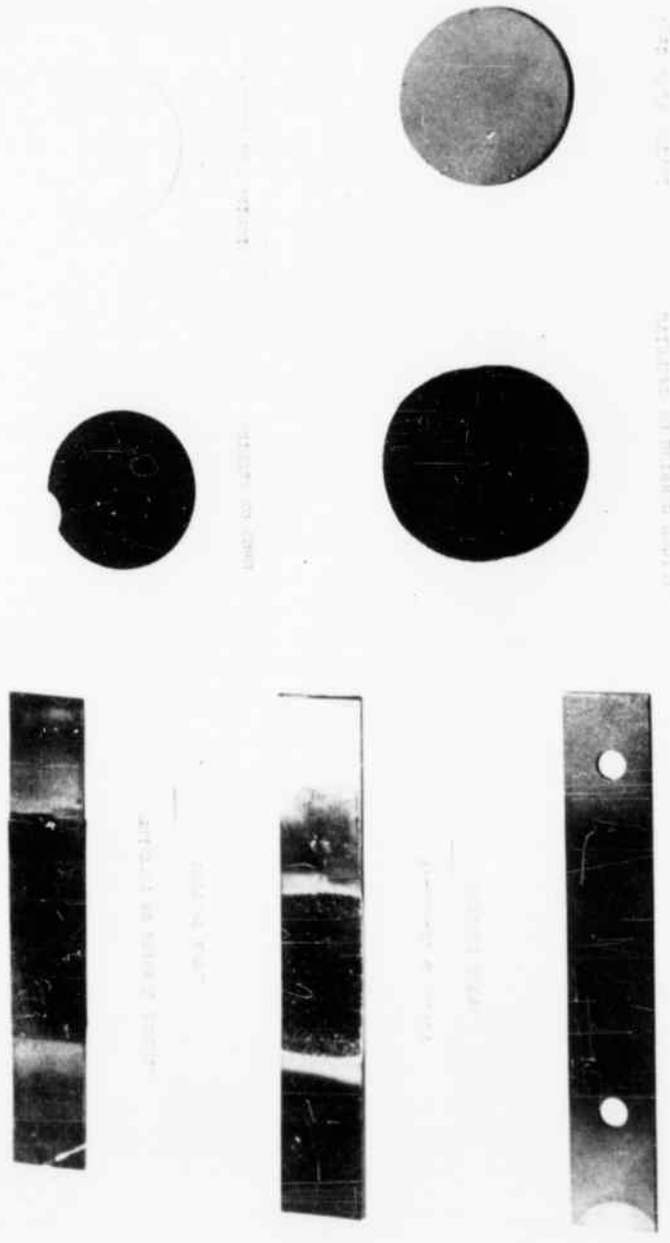

FIGURE 5 - Typical Specimens for Measurement of Emittance

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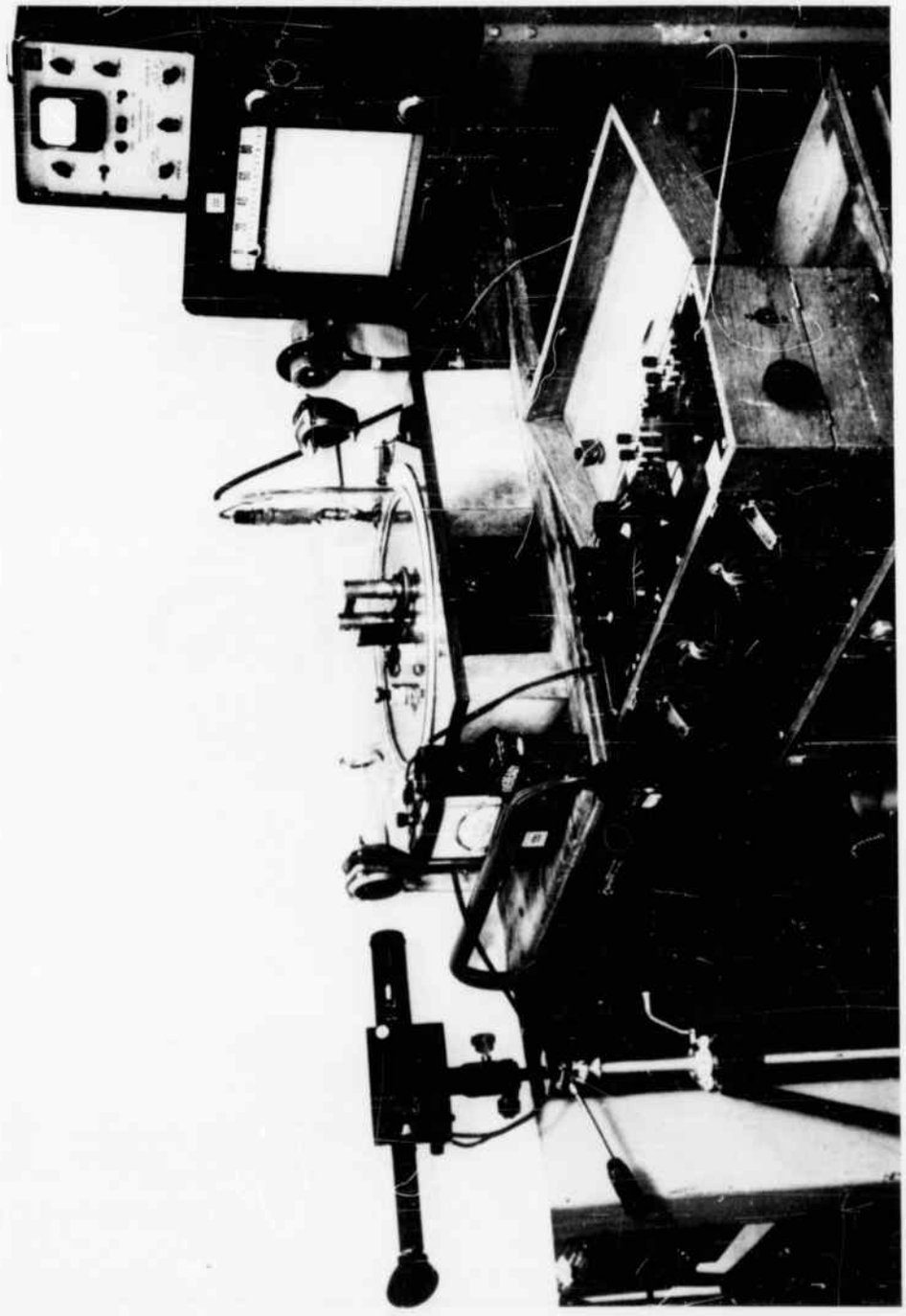

FIGURE 6 - Emittance Measurement Apparatus

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Reference: R-11064

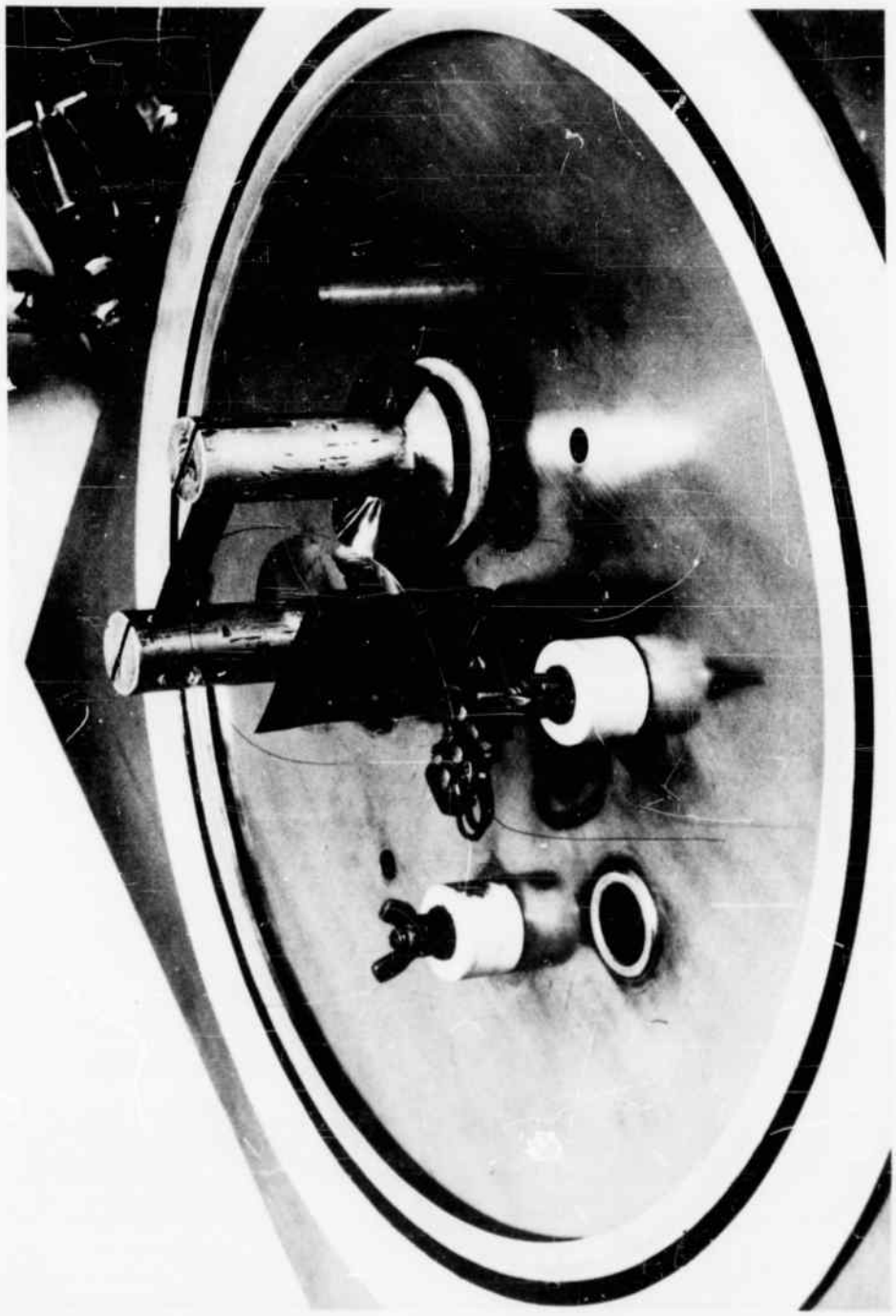


FIGURE 7 - Specimen Installation for Emittance Measurements

Reference: R-11065

Reference: R-11201

TOTAL EMITTANCE OF TANTALUM WITH VARIOUS COATINGS
VACUUM TESTS

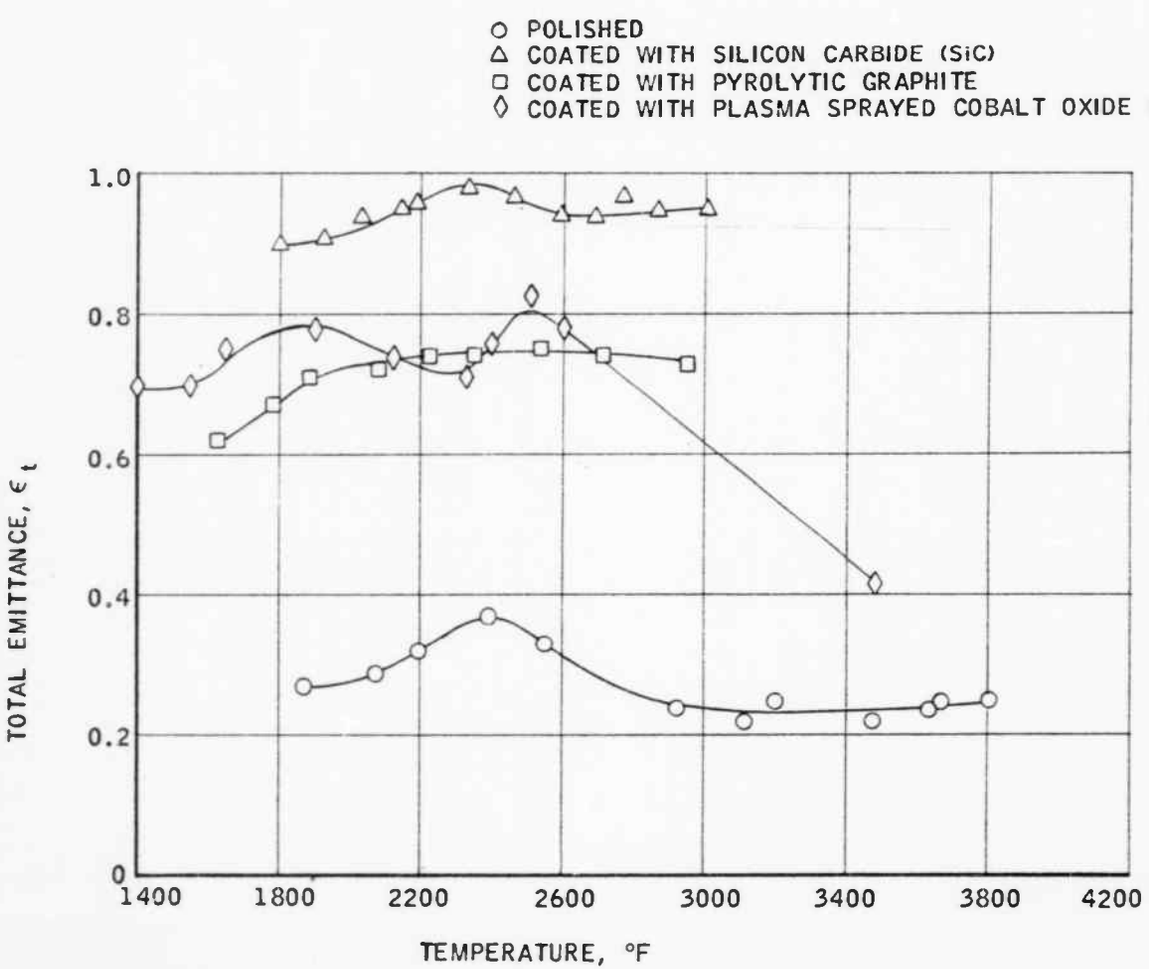
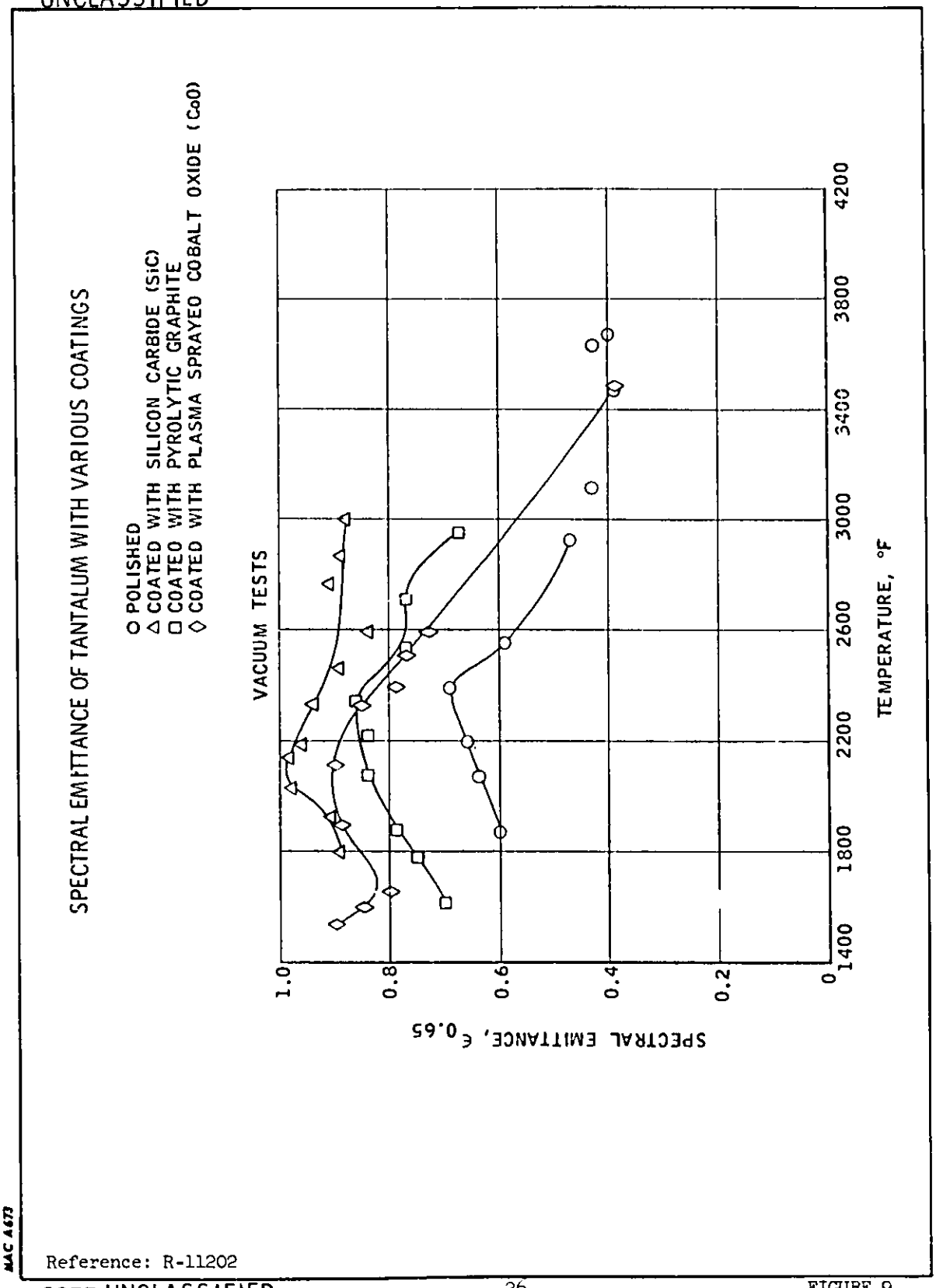


FIGURE 8



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Reference: R-11202

Reference: R-1120J

TOTAL EMITTANCE OF 6AI-4V TITANIUM ALLOY
POLISHED, AND COATED WITH ROKIDE "C"

OPEN SYMBOLS - ASCENDING TEMPERATURE ○- POLISHED

SOLID SYMBOLS - DESCENDING TEMPERATURE △- COATED WITH ROKIDE "C"

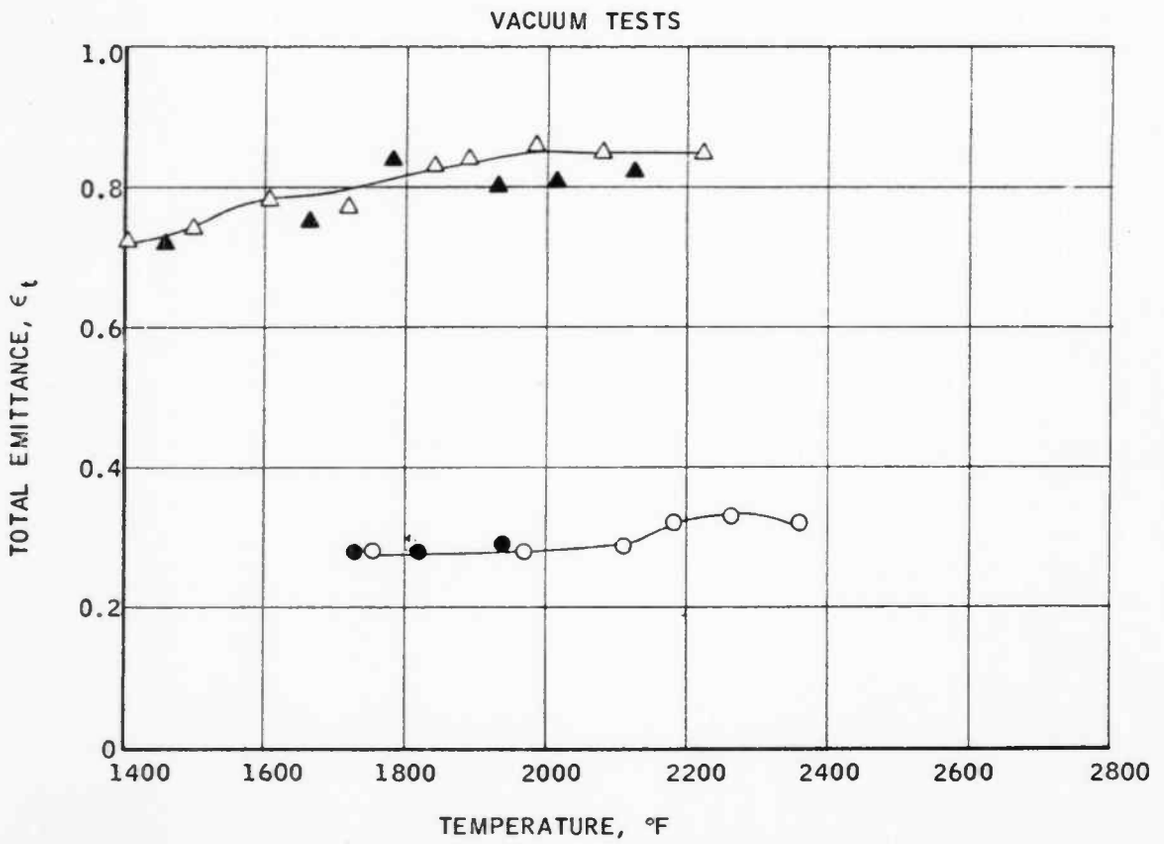

FIGURE 10

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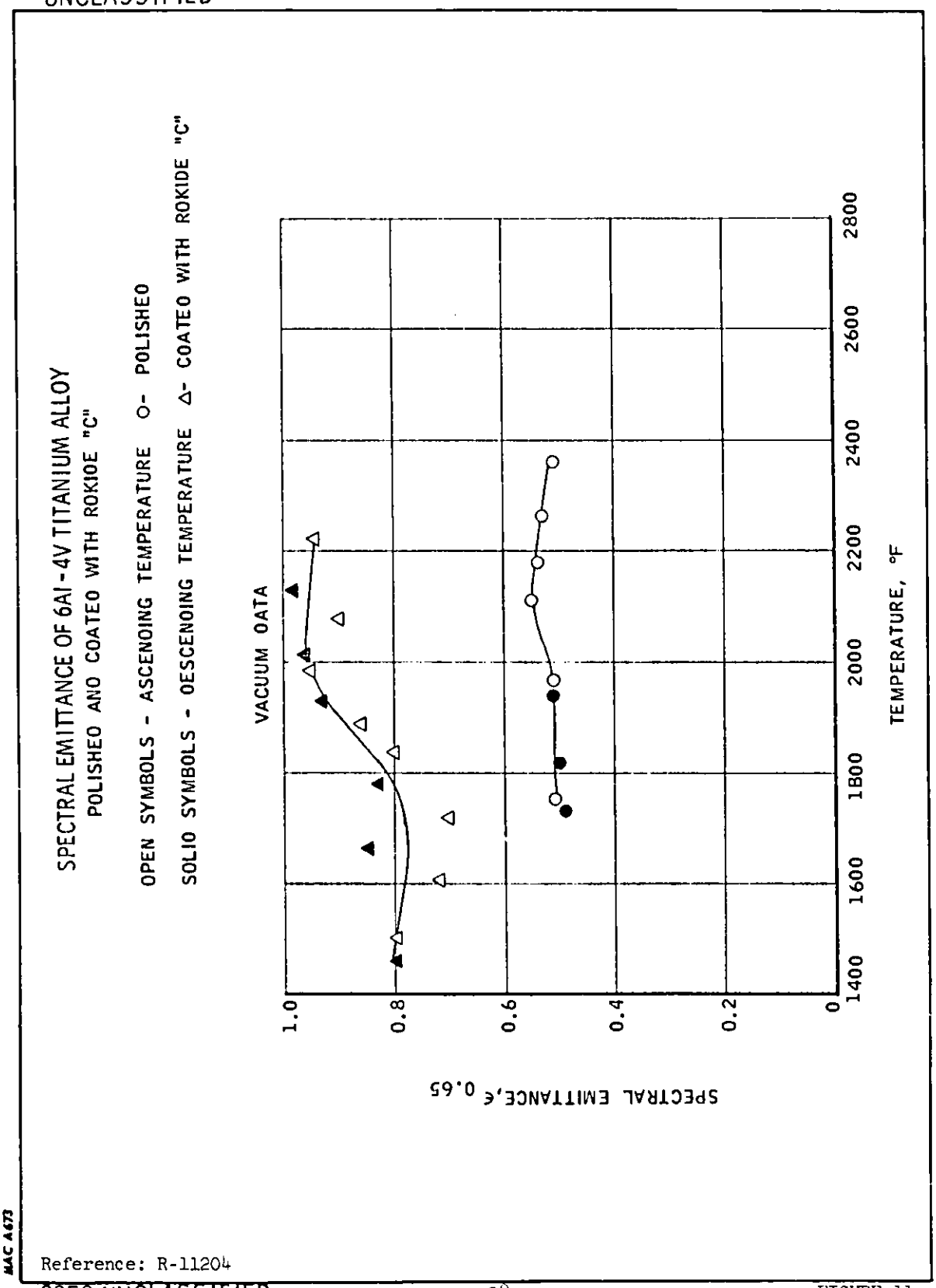

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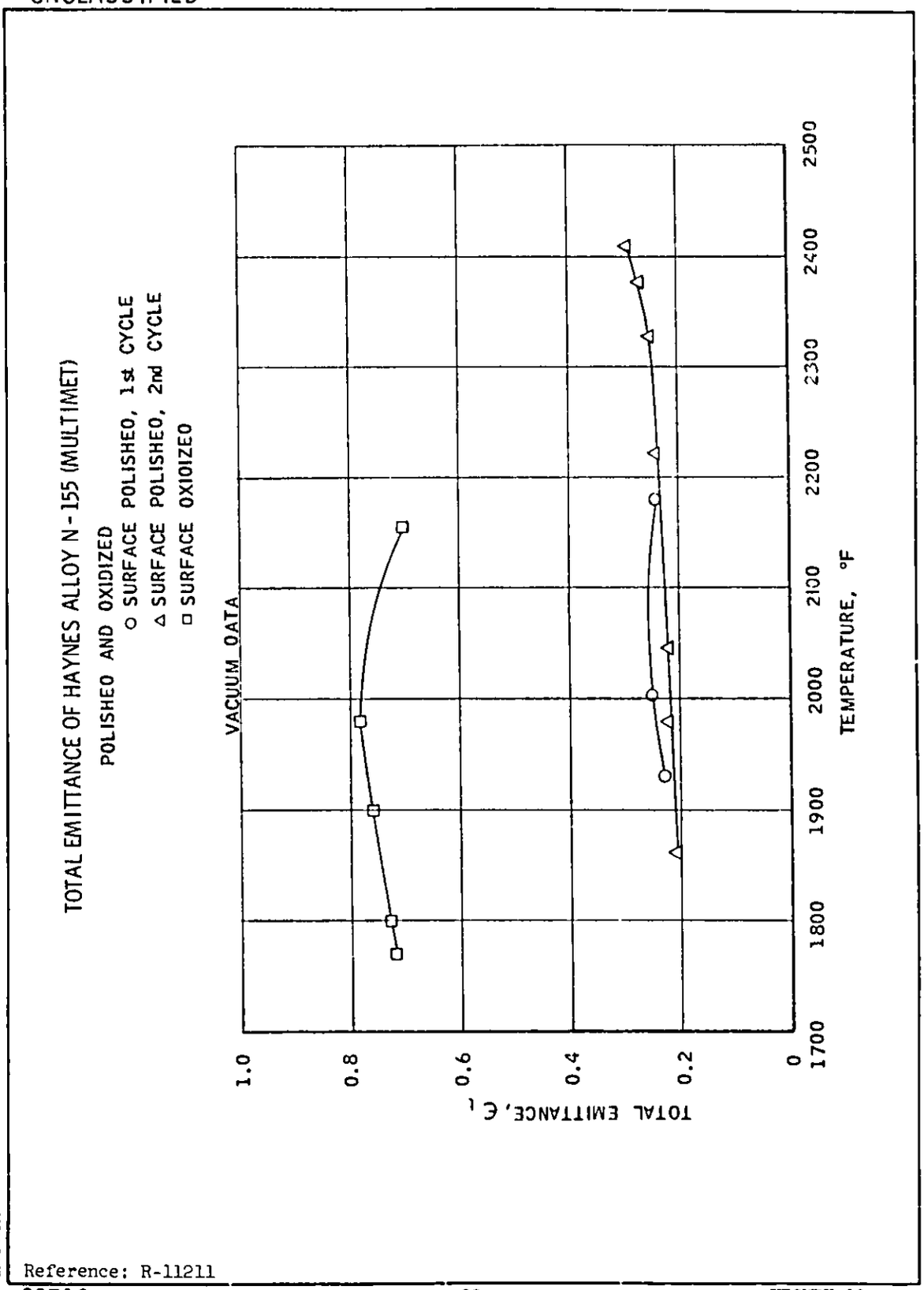
Reference: R-11204

FIGURE 11



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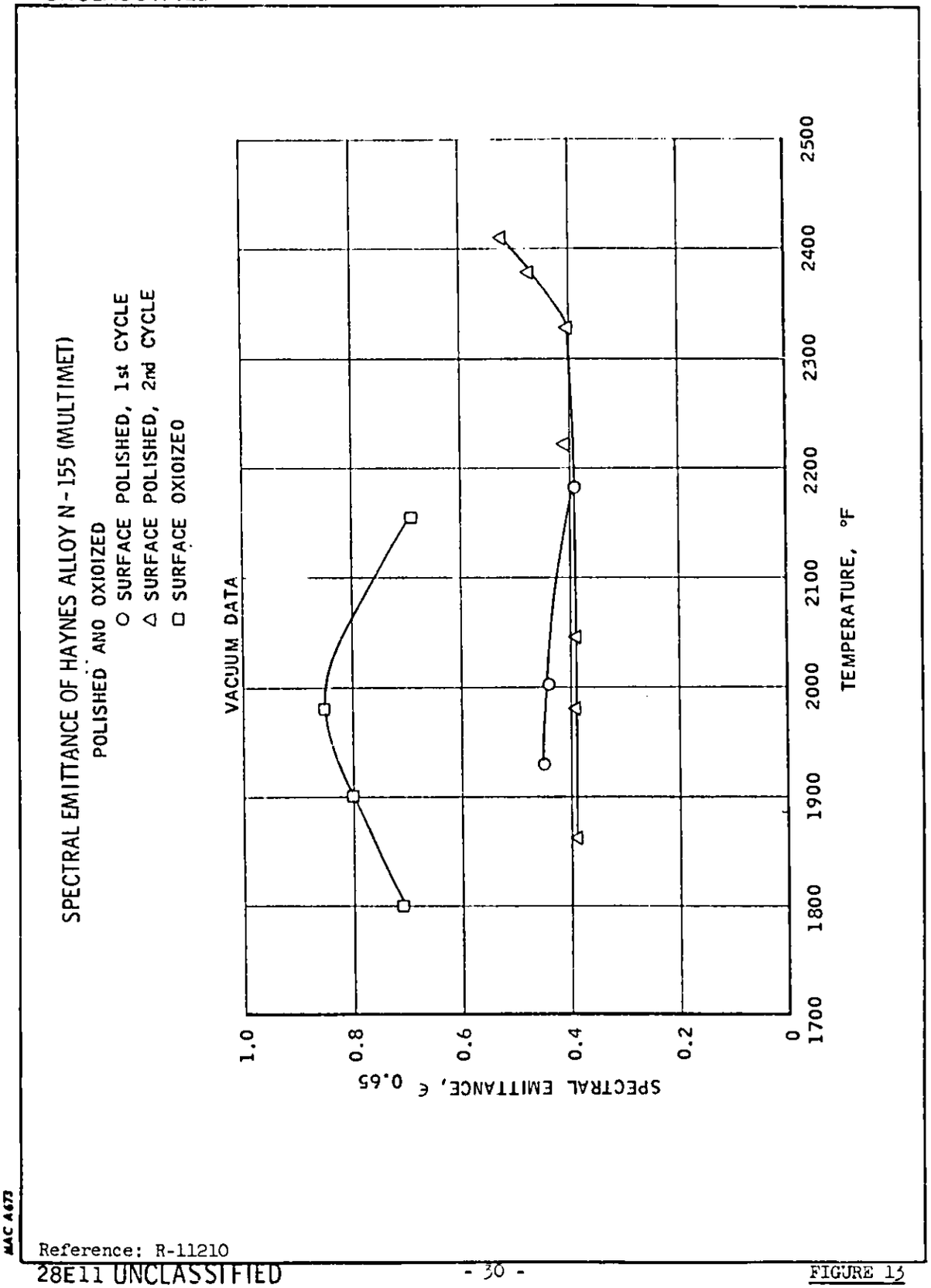
Reference: R-11211

FIGURE 12



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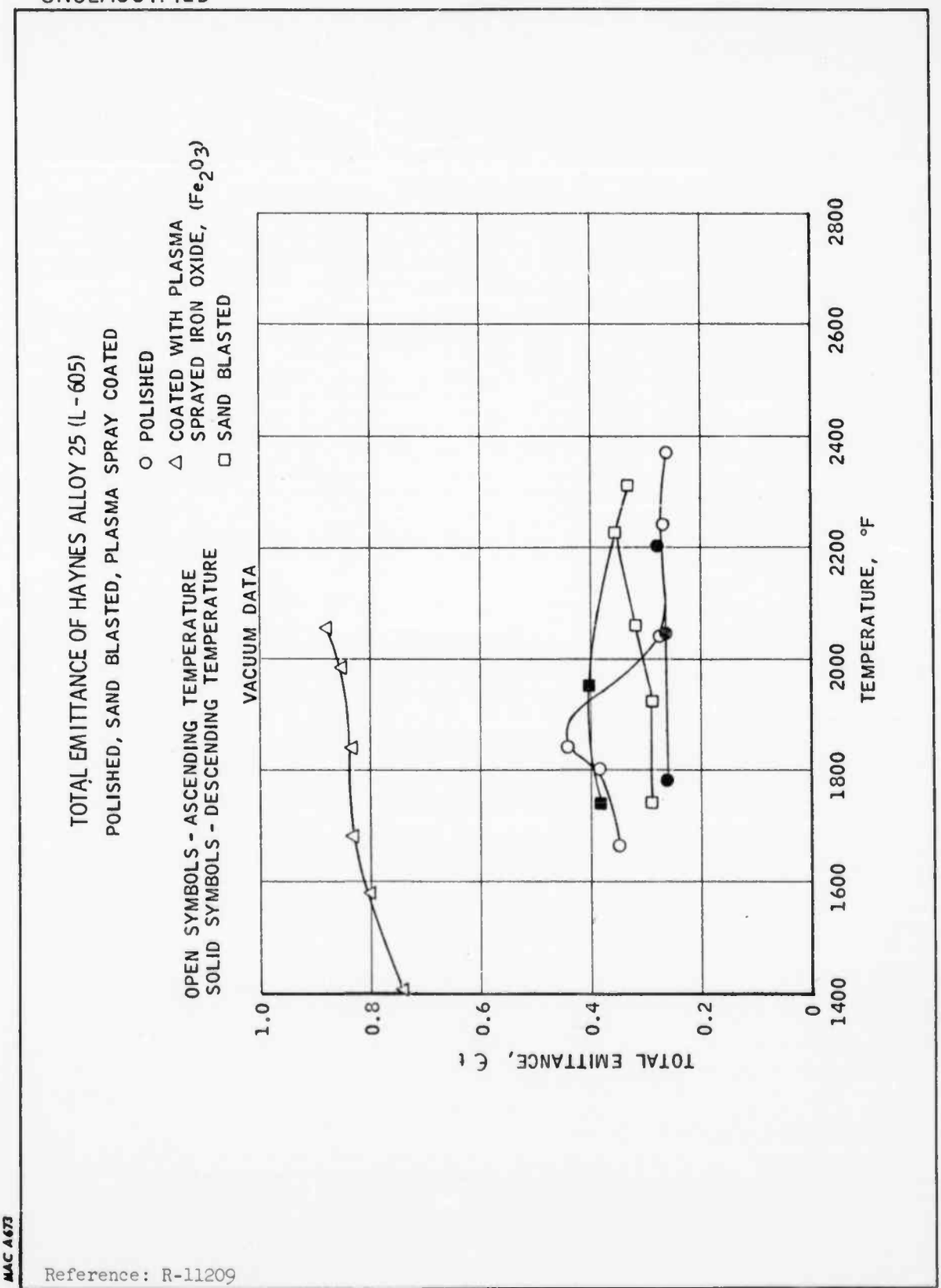
Reference: R-11210



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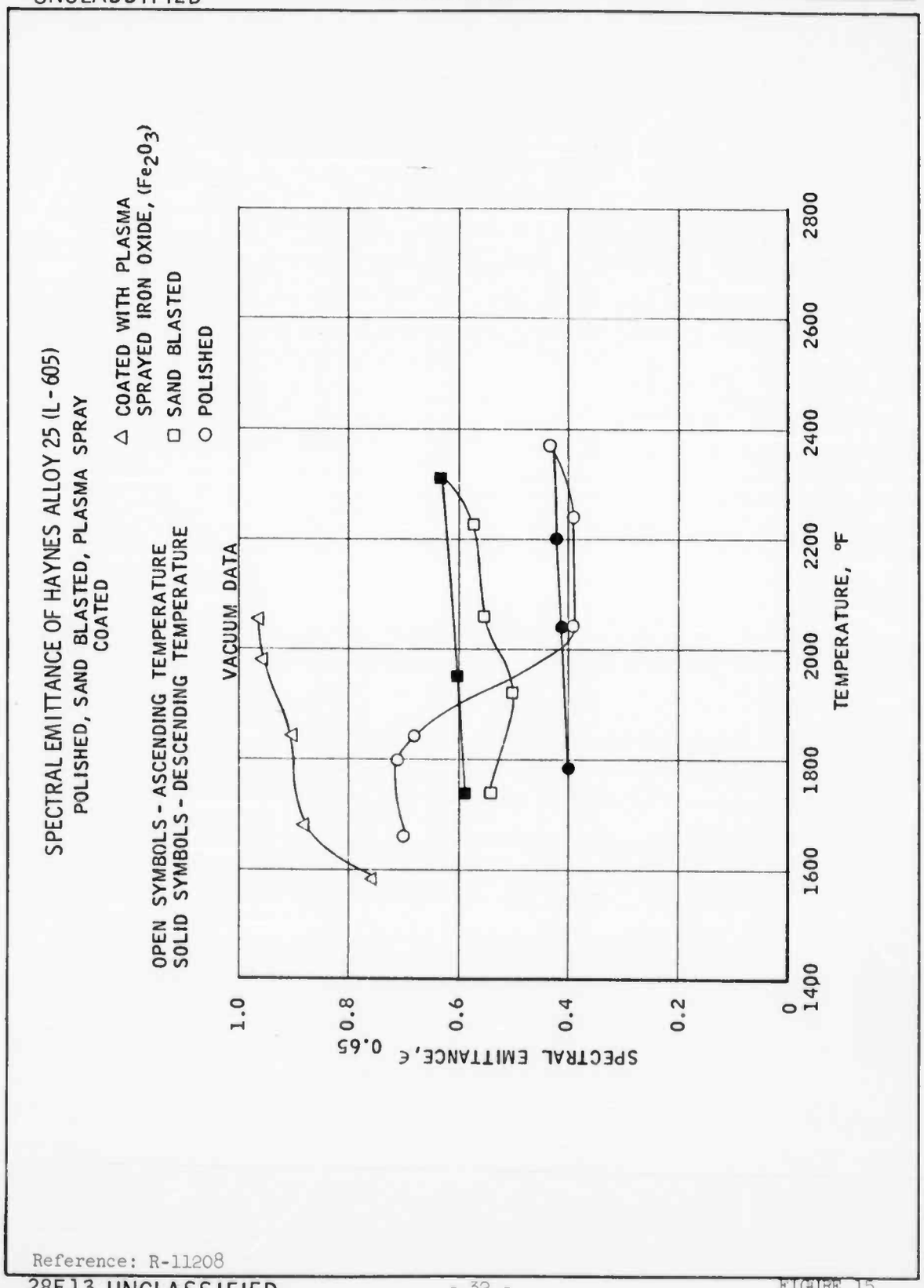
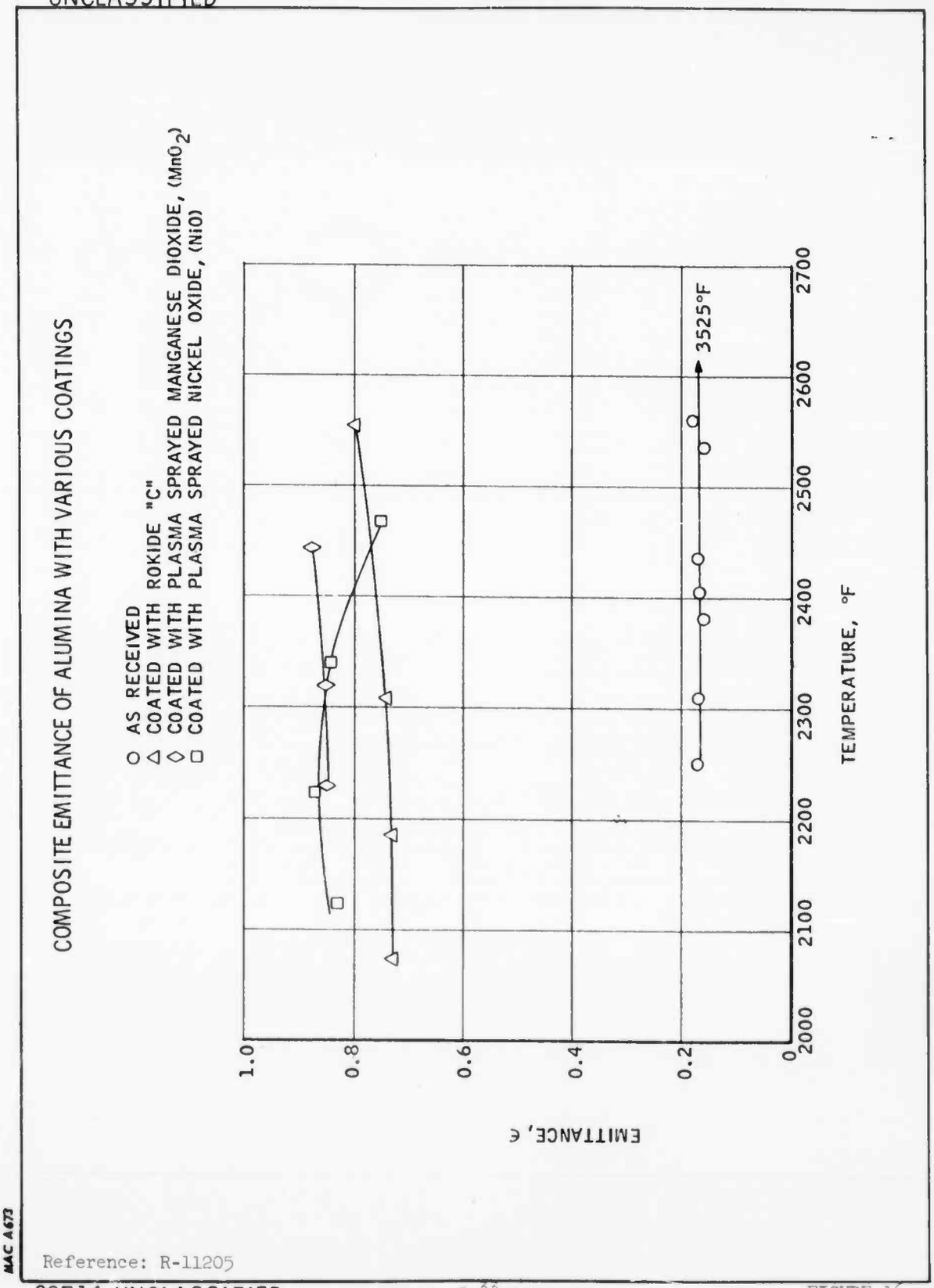
Reference: R-11209

FIGURE 14



Reference: R-11208



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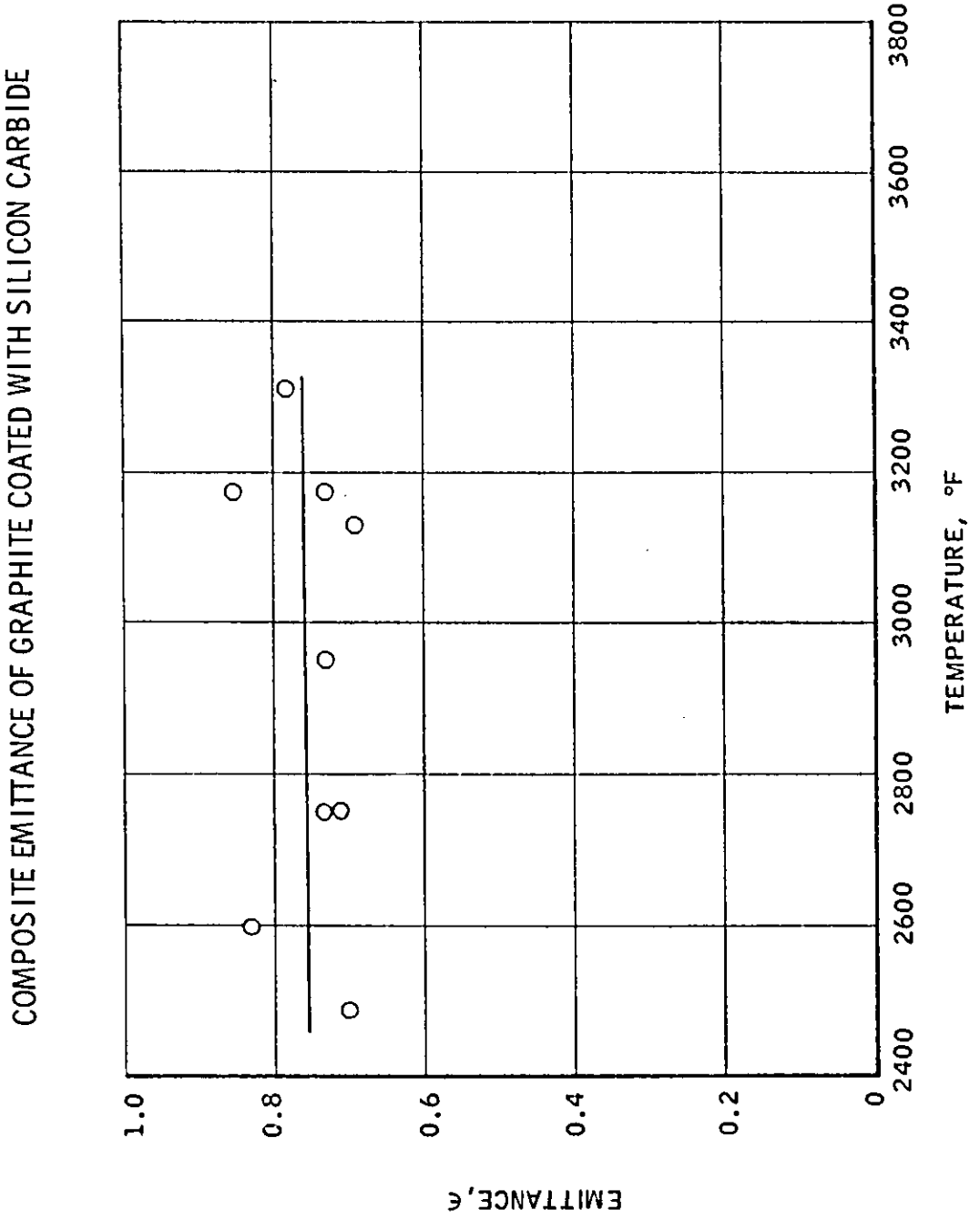
Reference: R-11205

FIGURE 16



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Reference: R-11206

FIGURE 17

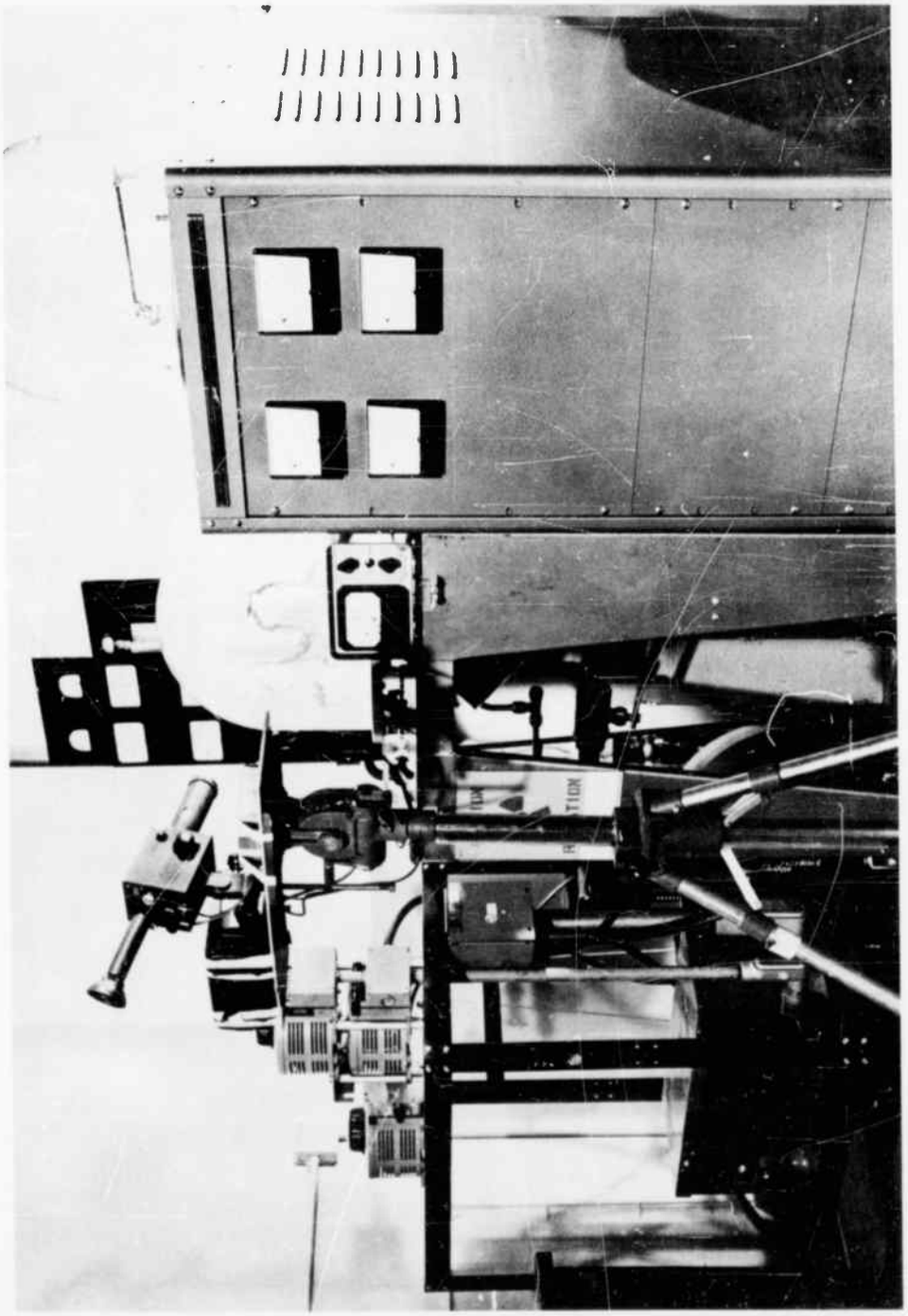

FIGURE 18 - Vapor Deposition Equipment for the Application of Anisotropic Coatings

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Reference: R-7779

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